Standard Operating Procedure for Analysis of Total Organic Carbon in Sediments (Dry Combustion, IR Detection)

LG601

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1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of Total Organic Carbon (TOC) in sediments.

1.2 This method is based on the infrared detection of CO_2 during dry combustion.

1.3 The approximate working range is 0.1% to 62% of carbon. This range can be extended to 99% of carbon.

2.0 SUMMARY

2.1 Total carbon in sediments is determined by dry combustion with a non dispersive, infrared carbon analyzer.

2.2 Sediments that contain inorganic carbon are first treated with phosphoric acid to destroy the inorganic carbon and then analyzed for total carbon.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Sediment samples are collected during Great Lakes Limnology surveys. Samples should be stored in glass jars with tight fitting Teflon lined lids at 4°C.

3.2 Amount of a sample collected should be sufficient to ensure a representative sample and allow for replicate analysis.

4.0 INTERFERENCES

4.1 Some forms of inorganic carbon (i.e., Dolomite) may be difficult to remove from the soil by acid treatment. Incomplete removal inorganic carbon will lead to high bias in the TOC results.

4.2 Care must be taken to ensure that adequate time is given to the treatment process to facilitate complete removal of inorganic carbon, especially for those soils suspected of having a high inorganic carbon content.

5.0 SAFETY

5.1 Safe laboratory procedures should be followed at all times.

5.2 All reagent preparation must be performed under a fume hood.

5.3 A current awareness of OSHA regulations regarding the safe handling of the chemicals specified in the SOP is recommended. A reference file of Material Safety Data Sheets (MSDS) must be maintained by the Health and Safety Officer and must be made available to all personal involved in the chemical treatment and/or analysis.

5.4 The following chemicals have the potential to be highly toxic or hazardous, consult the MSDS.

5.4.1 Hydrochloric acid (HCl)

5.4.2 Phosphoric acid (H_3PO_4)

6.0 EQUIPMENT AND SUPPLIES

6.1 LECO SC 444 non - dispersive, infrared carbon/sulfur analyzer.

6.1.1 Balance, interfaced with system software (LECO part # 751-300) or equivalent capability, ± 1 mg

6.1.2 Autoloader Kit (LECO part # 606-250-110)

6.1.3 Combustion Boats (LECO part # 529-203-150)

6.1.4 Printer, Okidata Microline 320 (LECO part # 601-480) or equivalent

6.2 Glassware and Accessories

6.2.1 Volumetric flasks and stoppers

6.2.2 Large culture tubes: 25 x 200 mm with Teflon-lined screw caps (Corning part # 986-25x) or equivalent

6.2.3 Teflon reagent bottles and Teflon-lined caps

6.2.4 Large and small porcelain crucibles

6.2.5 Small Teflon stir bars

6.2.6 Glass or metal sample/reagent scoop

6.2.7 Mortar and pestle, or automatic grinder

6.2.8 Sieve: 100- or 140-mesh

6.3 Analytical balance, capable of weighing to 0.0001 g

6.4 Evacuated desiccator with silica gel as desiccant

6.5 Multi-place stir/hot plate

6.6 Oven: 60°C, 105°C

7.0 REAGENTS AND STANDARDS

7.1 Reagent Preparation

Use reagent water for all solutions.

All reagent should be stored in glass or Teflon reagent bottles.

7.1.1 **Reagent 1: 4N Hydrochloric Acid (HCl)**

To a 1-L volumetric flask, add about 500 mL DI water. Slowly add 335 mL of concentrated hydrochloric acid. **Caution: Fumes!** Dilute to the mark, stopper, and mix by inversion.

7.1.2 **Reagent 2: 5% Phosphoric Acid (H_3PO_4)**

To a 200-mL volumetric flask, add approximately 100 mL DI water. Slowly add 10 mL of concentrated H_3PO_4. Dilute to the mark, stopper, and mix by inversion.

7.2 Preparation of Standards

All standards (calibration and quality control) are purchased either directly from LECO or from a manufacturer of certified standards.

7.2.1 **Standard 1:** Calibration Standard. Potassium Acid Phthalate - KHP ($KHC_8H_4O_4$). This standard contains 47% organic carbon

7.2.2 **Standard 2:** Calibration Control Standard (ICV or CCV). KHP (second source)

7.2.3 **Standard 3:** Sensitivity Check Standard (SCS). Certified soil standard

7.2.4 **Standard 4:** Soil Standard Reference Material (SRM)

8.0 PROCEDURE

8.1 Pretreatment

NOTE: *Only glass or metal is allowed to contact the sample. Reagent used during sample pretreatment must only contact glass or metal.*

All samples and SRM should be pretreated for inorganic carbon.

8.1.1 Sieving and Grinding Samples

8.1.1.1 Place the sample (approximately 10 g to 15 g) in a small crucible and cover.

8.1.1.2 Place the crucible in an oven at 60°C overnight. Some samples may take longer to dry. Check one sample for constant weight per batch of samples dried.

8.1.1.3 Allow the sample to cool. Place the entire sample in either an automatic grinder for homogenization or homogenize manually with mortar and pestle.

8.1.1.4 Once homogenization is complete, sieve the ground sample through a 100- or 140-mesh sieve. The portion of the sample which passes through the sieves will be treated.

8.1.1.5 Transfer the sieved sample to a 25 x 200 mm culture tubes and screw the cap on tightly.

8.1.2 Inorganic Carbon Test

8.1.2.1 Place a small aliquot (approximately 1 g) of sample on a watch glass.

8.1.2.2 To this aliquot add 1 - 2 mL of 4 N HCl and observe for effervescence. Record observation on the Sample Treatment Log Sheet.

8.1.2.3 If effervescence is detected, or the sample is suspected of having inorganic carbon present, the sample must be treated with 5% H_3PO_4 before analysis.

8.1.3 Treatment with 5% H_3PO_4

8.1.3.1 Dry large crucibles at 450°C for four hours. Weigh them and record the weight.

8.1.3.2 Add the sample to a crucible. Record the weight of the sample and crucible. If the sample is a spike, two weights should be entered: 1) the weight of the sample (approximately 0.200 g) and crucible and 2) the weight of the spike added (approximately 0.200 g).

8.1.3.3 Weigh all of the samples in this manner.

8.1.3.4 Add 1 mL of 5% H_3PO_4 to the sample in the crucible. Observe for effervescence.

8.1.3.5 Place the crucible on stir/hot plate with a Teflon stir bar and begin wetting the sediments slowly on low heat setting with mixing.

8.1.3.6 Once the entire soil is wet take the crucible from the plate and add 1 mL of 5% H_3PO_4. Observe for effervescence.

8.1.3.7 Continue as in section 8.1.3.4 until effervescence is no longer evident. Record the amount of acid added.

8.1.3.8 To the slurry in the crucible add four times the amount of DI water relative to the amount of acid added.

8.1.3.9 Place the crucible back on the stir/hot plate and mix completely on the low heat setting for 1 to 2 minutes. After mixing is complete, place the crucible on an oven safe pan and place in the oven at 60°C overnight.

8.1.3.10 Take the samples out of the oven and allow samples to cool in a desiccator until the time of analysis.

8.2 Analysis and Final Report Generation

NOTE: *This SOP will only address the portion of sample analysis that will allow the analyst to enter the instrument software, identify samples, log in samples, load samples onto the autoloader assembly, edit, and output results. This SOP will not cover system configuration or method set up. Any questions regarding the system format and method set up not covered in this section, refer to the LECO SC 444 Carbon/Sulfur Analyzer Instruction Manual.*

8.2.1 At this point, all untreated samples should be in culture tubes and all treated samples should be in crucibles in the desiccator.

8.2.1.1 The treated samples should be weighed and the weight recorded.

8.2.1.2 Scrape the sample from the sides of the crucible with the metal spatula. Grind the hardened sample to the fine particle size. Try to incorporate as much of the sample from the sides of the crucible into the final ground sample as possible.

8.2.1.3 Once all treated samples have been homogenized as in section 8.2.1.2, all the samples (treated and untreated) are ready for analysis on the LECO SC 444.

8.2.2 The main power to the LECO SC 444 should always remain on. **NEVER TURN THE MAIN POWER OFF**.

NOTE: *The instrument requires one half hour to warm up.*

8.2.3 To bring the main menu on the screen simply touch the screen anywhere and the main menu will appear.

8.2.4 Select the METHOD icon. Using the arrow keys on the keyboard, highlight the method to be used [TOC-SOIL Method, (High Level CARBON Analysis-Soil Matrix)]. Touch PRINT METHOD to receive a print out of the method information and the parameter values. Touch ESC.

8.2.5 From the main menu touch CALIBRATE. From the calibration menu touch EDIT CALIBRATION. Touch SELECT ELEMENT (Carbon). Touch PRINT to receive a printout of the calibration information and the applicable range. To return to the main menu, touch ESC twice.

NOTE: *The calibration procedure is outlined in section 8.3. The instrument is quite stable and should not have to be recalibrated unless an ICV and/or CCV fails (greater than ± 10% of the true value) or when a different calibration range is needed.*

8.2.6 From the main menu touch the ANALYZE icon. From the analyze screen touch SELECT ID CODE. The ID code screen will allow the analyst to add, delete, or modify the ID codes. If the samples or standards are to be analyzed for the first time on this instrument touch ADD ID CODE.

NOTE: *Standards that are to be used for calibration will be added in the CALIBRATE menu and will automatically appear on the sample ID code screen. All other standards can be added here. Please see sections 8.3.1 for the calibration standard definition procedure.*

8.2.7 If the samples have already been logged in, but ID codes need to be modified or deleted, use the arrow keys to highlight the ID CODE and then touch MODIFY ID CODE or DELETE ID CODE respectively. If modifications are made, the software will prompt the analyst to save changes. Select OK to save changes. If the highlighted ID code is to be deleted the software will prompt the analyst to confirm the decision.

8.2.8 Once all samples have been added to the ID code screen and all modifications, if any, have been made, highlight the ID code that appears first on the sample weight screen in the analyze menu. Touch ESC to return to the analyze screen.

8.2.9 On the analyze screen touch the ANALYZE box on the bottom of the screen. A pop up screen will appear. Make sure that the correct starting position on the rack is highlighted. Touch ANALYZE on the pop up screen to start the analysis.

8.2.10 To abort or reset the analysis during an analysis run, touch the ABORT ANALYSIS box at the bottom of the screen. On the pop up screen touch ABORT or RESET. Please see the LECO SC 444 Instruction Manual for further details.

NOTE: *If the analysis is aborted while a combustion boat is in the furnace the instrument will display and save the result, but the result will be incomplete. Whenever an analysis is aborted the instrument should be allowed to sit for 1 to 2 minutes and a blank should be run before sample analysis is resumed.*

8.2.11 When the analysis run is complete (no more sample IDs or weights appear on the weights list on the analyze screen) touch ESC.

8.2.12 Touch the REPORTS icon from the main menu. Touch the RESULTS icon on the report's menu. A list of results will appear. Each result will have a number next to it that will correspond to the run number.

8.2.12.1 Touch the NEXT FIELD box at the bottom of the screen to toggle among the different screens available for report output format. Once the format is chosen use the arrow keys to move from one result to the next until it is pointing at the result to appear in the report. Touch INCLUDE RESULT to highlight the result. Continue until all the results to appear in the report are highlighted. If an error is made and an incorrect result is highlighted, use the arrow keys to move the pointer to that result and touch EXCLUDE RESULT to remove the highlight.

8.2.12.2 Once the results that are to appear in the report have been highlighted, touch PROCESS RESULTS. A pop up screen will appear. On this screen touch the box next to PRINT RESULTS and then touch OK. The results will print in the format chosen above.

8.2.13 After the results have been printed, touch ESC twice to return to the main menu.

8.2.14 The analyst can now log off the instrument by simply touching the LOGOFF icon.

NOTE: *The combustion boats are EXTREMELY HOT after ignition. To avoid being burned allow the boats to cool in the boat collection bin. When the boats have cooled, the collection bin can be removed from the autoloader assembly and the boats can be put aside until they can be cleaned for later use. The combustion boats can be cleaned and reused up to four times. If the boat is difficult to clean, discard.*

8.3 Instrument Calibration

The instrument will only need to be calibrated when an ICV and/or a CCV fails or when a different calibration range is required.

8.3.1 Touch the screen to activate the main menu. From the main menu touch the CALIBRATE icon. From the calibrate menu touch the DEFINE STANDARDS icon. From this screen standards can be added, deleted, or modified.

8.3.1.1 To add a calibration standard to the list touch ADD STANDARD. A window appears which allows the analyst to enter a new standard ID code, lot number, % sulfur of sulfur standard and % carbon of carbon standard. When all the values have been entered, touch OK to add the standard to the standards list.

8.3.1.2 To delete or modify a calibration standard use the arrow key to highlight the standard then touch DELETE STANDARD or MODIFY STANDARD. A pop up window will appear which will confirm the deletion or display the ID code for editing.

8.3.1.3 Touch ESC twice to reach the main menu.

8.3.2 Touch the ANALYZE icon.

8.3.2.1 Continue as in sections 8.2.5 through 8.2.12. The calibration standard ID codes will appear on the ID code list automatically. Any modifications to the standards have to be made through the define standards menu.

8.3.2.2 The calibration will consist of 4 weights of calibration standard (i.e., approximately 0.050 g, 0.075 g, 0.100 g, and 0.150 g). Each of these weights will be analyzed three times.

8.3.2.3 After the analysis of the calibration standards, touch ESC. From the main menu touch the CALIBRATE icon. From the calibrate menu touch STANDARD CALIBRATION. A list of results will appear. Each result will have a number next to it that will correspond to the run number. Choose the median result to enter for the calibration point. Use the arrow keys to move the pointer to this result and touch INCLUDE RESULT. Continue until 4 results have been included (one for each calibration weight). Touch PROCESS RESULTS. A pop up window will appear with the calibration curve on it (touch SELECT ELEMENT to toggle between the curve for sulfur and carbon). Touch ESC. The software will prompt the analyst to save the calibration. Save the calibration. The software will prompt the analyst for the type of curve and intercept. Choose linear and fixed respectively. The software will prompt the analyst to enter the intercept. At this point the intercept should be entered as 0.0000.

8.3.2.4 Exit to a main menu, touch ANALYZE, touch SELECT ID CODE. If a blank has not been added to the ID code list, add it now (see section 8.2.6). Analyze 3-5 blanks. The blank weights should correspond to the middle weight of the standard used for calibration (i.e., 0.100 g). After all the blanks have been analyzed go to the standard calibration menu. Recalibrate the instrument using the previous standard values and the new intercept (the average value of the blanks analyzed above). Save this calibration.

9.0 QUALITY CONTROL

9.1 The following items are required with the minimum frequency indicated.

QC Sample Type		Frequency	Acceptance Criteria
External	Lab Duplicate (LD1)	Approximately 10% of samples collected in duplicate	RPD $\leq$ 20% (interim limit)*
	Field Duplicate (FD1)	Approximately 10% of samples collected in duplicate	*
Internal	Round Robin Standard Lab Sediment	Determined by the lab	*
	Matrix Spike (MS)	During each batch or 1 per 40 samples, whichever is more frequent	100% ± 20%

* Acceptance criteria for these QC samples is based on laboratory performance.

10.0 CALCULATION

Treated samples result calculation:

$$Result\ (\%\ Carbon) = Sample\ Result\ (\%\ Carbon) \times Correction\ Factor$$

$$Correction\ Factor = \frac{Final\ weight\ of\ crucible\ and\ soil - Weight\ of\ crucible}{Initial\ weight\ of\ crucible\ and\ soil - Weight\ of\ crucible}$$

10.1 Percent Recovery (%R) Calculations for ICV, CCV, and ISC

$$\%\ Recovery = \frac{\%\ Carbon\ Found}{True\ \%\ Carbon} \times 100$$

10.2 Relative Percent Difference (RPD) for Duplicate:

$$RPD\ (\%) = \frac{\left| Sample\ Result - Duplicate\ Result \right|}{\left(\frac{Sample\ Result + Duplicate\ Result}{2} \right)} \times 100$$

10.3 Percent Recovery for Matrix Spike:

$$Matrix\ Spike\ Recovery\ (\%) = \frac{\%\ Carbon\ Found}{Calculated\ \%\ Carbon} \times 100$$

$$Calculated\ \%\ Carbon = \frac{(Weight\ of\ Sample \times \%\ Carbon) + (Weight\ of\ Spike \times \%\ Carbon)}{Total\ Weight}$$

11.0 PREVENTIVE MAINTENANCE

11.1 Please refer to the LECO SC 444 Instruction Manual under the Maintenance, Diagnostics and Service sections for trouble shooting and routine preventive maintenance.

12.0 REFERENCES

12.1 LECO. 1992. LECO SC 444 Sulfur/Carbon Analyzer Instruction Manual.

12.2 Standard Operating procedure for the Analysis of Total Organic Carbon in Soils. Method 415 soil.

13.0 ADDITIONAL NOTES

13.1 GLNPO's Standard Operation Procedure for Analysis of Total Organic Carbon in Sediments (dry Combustion, IR Detection) and the CRL SOP: AIG009 are the same SOP with one exception the GLNPO SOP calls for samples to be collected in wid-mouthed plastic jars with polypropylene lids and the CRL SOP requires samples to be collected in glass bottles with teflon lined caps.